A chamber for the *in-situ* IR measurement of C_{60} thin films while doping with alkali metals

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A sample chamber has been designed to simultaneously measure the DC resistivity and IR transmission of C_{60} thin films while the films are doped with alkali metals *in-situ*. The chamber construction allows a choice of windows to cover the entire IR and visible range, while x-ray diffraction studies are also possible to determine the sample stoichiometry.

C_{60} has been found to be a superconductor at low temperatures when doped with alkali metals.[1] The sample chamber design described here is notable in that it allows one to continuously take IR transmission spectra of C_{60} thin films as the films are slowly doped. In addition, the chambers are durable and small enough that they can be cooled to measure the superconducting transition of the doped films, which can then be further characterized by x-ray diffraction, in the same chambers.

The sample chambers must be constructed to enable the sample to reach temperatures up to 125°C and so increase the diffusion rate of the dopant. The doping process itself is controlled by independently adjusting the temperature of the alkali dopant to change its vapor pressure. These requirements are met by chambers made of Pyrex glass and are drawn to scale in Fig. 1. The central section is fabricated from 11 mm OD, 1.5 mm wall tubing and is approximately 1 cm high. Two vacuum tight IR windows are sealed to the tube. The upper window also serves as a substrate on which C_{60} is deposited by sublimation. Of the two 6 mm OD glass tubes attached to the central section as shown, the stem serves to pump out the chamber and is sealed off after the C_{60} and alkali metal are evaporated. The appendage on the left contains the alkali metal, evaporated on the inside surface of the bulb. The "neck" between the bulb and the chamber features a small restriction to trap a 3/16" stainless steel ball bearing in the bulb. When actuated by a magnet, the ball bearing serves as an effective valve to isolate the C_{60} film from the alkali metal vapor.

Key to the IR transmission experiments was the choice of window material. High resistivity (> 1000 $\Omega$$-$cm), 15 mil thick, silicon wafers were obtained from Virginia Semiconductor, Inc.[2] and cleaved into 1/2" squares. High resistivity silicon is essential since the silicon serves not only as the chamber window, but also as the sample substrate and so should have a high resistivity compared to the M_xC_{60}. The polished wafers are ground on one side with #220 grit emery paper to eliminate fringing in the IR spectrum. A platinum ink pen is used to draw a 4-terminal lead pattern directly on the silicon. After firing at 500 °C for a few minutes, a pure platinum film is left where the ink was placed.

The windows are then attached to the chemically cleaned and baked Pyrex chambers. Varian "Torr-Seal" is an effective high vacuum seal, but only when precisely mixed, and baked for at least 48 hours at 120−140 °C.[3] Prepared properly, the chambers maintain high vacuum exceptionally well, the best indicator of performance being the lifetime of evaporated Rb films.

In practice, a small chip of alkali metal is first loaded into the bulb of the sample chamber in an inert atmosphere glove box. The ball bearing is moved into the neck of the chamber, while the chamber is connected to a pumping system by its stem, through a single un-greased Viton O-ring in a compression fitting. The stem sticks out approximately 1.5" to allow the chamber to be sealed with a torch without burning the O-ring. Mounted inside the pumping system is a vacuum actuator with approximately 2" travel, supporting a small tantalum boat used to evaporate C_{60}. The boat is inserted through the chamber's pumping stem during evaporation and retracted before sealing. Electrical connections to the boat are made by conventional vacuum feedthroughs. The C_{60} is evaporated at a base pressure of 2×10^{-6} Torr or better. To monitor film thickness, visible light interference fringes are counted as pre-purified C_{60} is evaporated from the tantalum boat.

Next, the alkali metal is evaporated into a thin film, to remove any impurities trapped in the metal and improve its gettering properties by increasing the surface area. The ball bearing is held in the "closed" position by a magnet while a blow torch heats the glass bulb locally over the metal chip. After the glass cools, the ball bearing is removed for a final pump down, the boat is retracted from the stem, and the chamber is sealed. At this point, not only is the clean alkali metal available to dope the C_{60}, but it also continues to improve the chamber vacuum by gettering residual O_2 and H_2O.

When doping, the sample chamber is held vertically in a jig with the glass bulb in an electrically heated oil bath, and the IR windows at the focal point of a FTIR spectrometer. To heat the C_{60}, and so increase the diffusion rate of the alkali metal, a small copper block is attached to the C_{60} substrate. The block allows for passage of the IR beam and has a hole in which a small heater resistor is cemented. A 1/8" diameter, wire-wound, glass enameled 10Ω resistor is sufficient to heat the sample to at least 300°C.

As the C_{60} film is doped, the film color changes from a golden brown to a metallic grey, and is easily observed through the glass walls of the sample chamber. Doping is
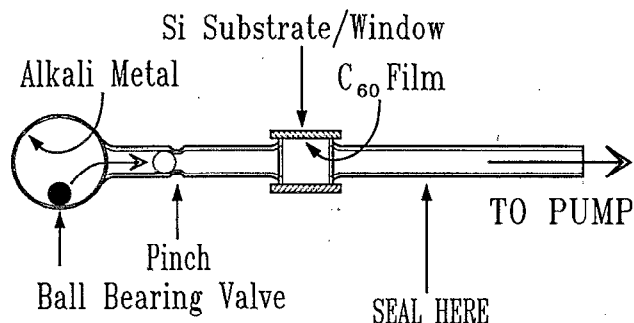
FIG. 1. The assembled sample chamber, with principle features labeled.

FIG. 2. X-ray diffraction spectrum of a pure C_{60} film approximately 2 μm thick, prepared in the same chambers as described in the text. The 15 mil. silicon windows are sufficiently transparent to observe the FCC structure of the polycrystalline film unambiguously.

also monitored more quantitatively using the technique first described by Kochanski et al.[4] Pristine C_{60} is an insulator, but as doping procedes its resistivity drops by 3 or more orders of magnitude, reaching a minimum at the M_3C_{60} phase. Further doping increases the resistivity until the $x=6$ band insulating phase is formed. Our C_{60} films are typically ~1 μm thick with resistance dropping from the 100 kΩ range to about 50 Ω near the minimum at a typical sample current of 10 μA. Note that, the resistance of the high resistivity silicon substrates is at least 3 orders of magnitude higher than that of the doped C_{60} film. DC conductivity of the films can also be inferred from the overall IR transmission, which typically drops by a factor of 5 or more.

The sample chambers as described were used to take continuous IR spectra of M_xC_{60} for $x=0-6$, M=Rb, K. An analysis of the data has been published elsewhere.[5] Some Rb_3C_{60} samples have been removed from the spectrometer and cooled to 4.2 K. The samples show a superconducting transition in resistivity at 28.5 K and the chambers survive repeated cycling between room temperature and 4.2 K.

A number of phases are observed in the M_xC_{60} materials.[6] It is therefore important to correlate the IR observations with in-situ phase identification. Figure 2 shows a powder spectrum of a typical undoped film, taken at the X3B1 beamline of the National Synchrotron Light Source at Brookhaven National Laboratories. The incident and diffracted beams were defined by 1 mm slits. At the wavelength used, $\lambda = 0.764$ Å, the transmission through the two silicon windows was approximately 50%. The spectrum shows resolution-limited (111), (220), (311), and (420) diffraction lines at their expected positions. From the Scherrer relation, the C_{60} grain size is at least 200 Å.

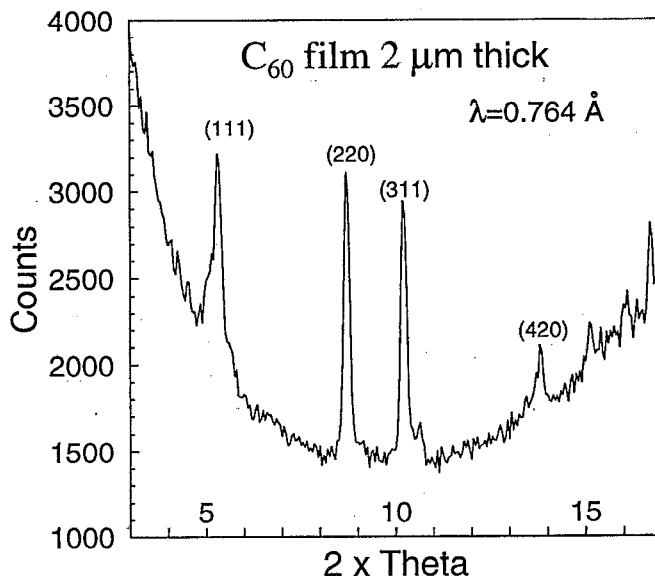Current efforts are concentrated on extending the operating temperature range of the sample chambers, pres-

ently limited by the vacuum epoxy seal. Hotter sample temperatures will help to increase sample homogeneity by increasing the diffusion rate of the dopant. It must be stressed that the chambers are not limited to the use of silicon windows. Glass and Quartz windows are easily substituted for visible and UV measurements respectively. As illustrated by the examples above, the small, rugged, coolable sample chambers described here are ideal for a wide variety of experiments on C_{60} and its air sensitive compounds.

ACKNOWLEDGMENTS

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